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Japanese Kokai Patent Application No. Hei 8[1996]-259773

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FLUORINE-CONTAINING POLYMER AQUEOUS DISPERSION,  
WATER-BASED PAINT CONTAINING THIS DISPERSION AND PAINTED MATERIAL

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Abstract

Objective

To obtain a fluorine-containing polymer aqueous dispersion  
that can provide a coating with excellent film-formation

properties, clear-coat transparency, binding and weather resistance, as well as high gloss and excellent mechanical characteristics.

#### Constitution

20-100 parts by weight of a monomer mixture containing an acrylate alkyl ester and/or methacrylate alkyl ester and an ethylenic unsaturated monomer is seed polymerized in the presence of 100 parts by weight of fluorine-containing polymer particles in an aqueous dispersion containing said fluorine-containing polymer particles, where said monomer mixture contains 0.5-45 wt% of a monomer having cyclohexyl groups.

#### Claims

1. A fluorine-containing polymer aqueous dispersion, characterized by being produced by subjecting 20-100 parts by weight of a monomer mixture containing an acrylate alkyl ester with a C<sub>1-18</sub> alkyl group and/or a methacrylate alkyl ester with a C<sub>1-18</sub> alkyl group, and an ethylenic unsaturated monomer that can copolymerize with these esters, to emulsion polymerization in an aqueous medium in the presence of 100 parts by weight of fluorine-containing polymer particles, where the average particle diameter of the particles of polymer obtained by said emulsion polymerization is 0.05-3  $\mu\text{m}$ , and a monomer having cyclohexyl groups is contained in said ethylenic unsaturated monomer in the amount of 0.5-45 wt% of said monomer mixture.

2. The dispersion described in Claim 1, where the aforementioned fluorine-containing polymer is a fluorovinylidene polymer.

3. The dispersion described in Claim 2, wherein the aforementioned fluorovinylidene polymer is obtained by the polymerization of a monomer mixture containing 70-95 mol% of vinylidene fluoride and 30-5 mol% of chlorotrifluoroethylene.

4. The dispersions described in any of Claims 1-3, wherein the aforementioned monomer having cyclohexyl groups is at least one type of substance selected from cyclohexyl acrylate, cyclohexyl methacrylate and cyclohexyl vinyl ether.

5. A water-based paint that contains any of the dispersions described in Claims 1-4.

6. A water-based paint containing any of the compositions of Claims 1-4 for the exterior or interior decoration of medium-level or low-level buildings.

7. A painted material, obtained by coating the water-based paint described in Claim 5 or 6.

#### Detailed description of the invention

[0001]

#### Industrial application field

The present invention concerns a fluorine-containing polymer aqueous dispersion that can provide a coating with excellent film-formation properties, clear-coat transparency, adhesion and weather resistance, as well as high gloss and excellent mechanical characteristics.

[0002]

More specifically, the present invention concerns a fluorine-containing polymer aqueous dispersion produced by subjecting a monomer mixture containing determinate amounts of an acrylate ester and/or a methacrylate alkyl ester and ethylenic unsaturated monomer for seed polymerization in the presence of particles of fluorine-containing polymer, where said fluorine-containing polymer aqueous dispersion is characterized in that a monomer having cyclohexyl groups is used as the ethylenic unsaturated monomer in a determinate amount. The present invention also concerns a water-based paint containing this dispersion and a painted material.

[0003]

Prior art

Fluorine-containing paints are used as weather resistant paints for decorating the exteriors and interiors of medium-level and low-level buildings. Various technologies have been developed for obtaining these types of fluorine-containing paints. Although fluorine-containing paints are often substances that can be dispersed in organic solvents, the use of organic solvents is problematic in terms of safety and environmental protection, and thus the use of aqueous materials is preferred. The types of methods described below are known methods for manufacturing aqueous dispersion compositions of fluorine-containing polymers.

[0004]

In Japanese Kokoku Patent No. Hei 4[1992]-55441 and Japanese Kokai Patent Application No. Hei 3[1991]-7784, methods are described whereby film-formation properties and film transparency that cannot be obtained from emulsion blends are obtained by carrying out the emulsion polymerization of an ethylenic unsaturated monomer in an aqueous medium in the presence of vinylidene fluoride (VdF) system copolymer particles. However, only hexyl methacrylate is indicated as an example of a (meth)acrylate ester with a C<sub>1-18</sub> alkyl group. There is no discussion of (meth)acrylate esters, vinyl ethers or acetate esters containing cyclohexyl groups having a cyclic hexyl structure, and neither is there discussion concerning adhesive properties.

[0005]

In Japanese Kokai Patent Application No. Hei 2[1990]-225550, an aqueous dispersion for weather resistant paint formed by the copolymerization of alkyl vinyl ether with fluoroolefin is described, and cyclohexyl vinyl ether is cited as an example of the alkyl vinyl ether. However, there is no mention or suggestion pertaining to the postpolymerization of the alkyl ester or pertaining to the improvement of base material adhesion by the postpolymerization of alkyl esters or by the copolymerization of cyclohexyl vinyl ether.

[0006]

Japanese Kokai Patent Application No. Hei 6[1994]-228491 describes the postpolymerization of a fluoroolefin copolymer to a resin aqueous dispersion produced by the copolymerization of alkyl vinyl ether with fluoroolefin, and more specifically, describes the use of cyclohexyl vinyl ether as a monomer for the fluoroolefin copolymer that is to be post-polymerized. However, the substance that is postpolymerized is the fluoroolefin copolymer, and the postpolymerization of non-fluorine alkyl esters alone is not discussed. In addition, there is no discussion or suggestion concerning the improvement of base material adhesion by the copolymerization of cyclohexyl vinyl ether.

[0007]

Problems to be solved by the invention

The present invention was developed in light of the aforementioned problems, and has the objective of obtaining a fluorine-containing polymer aqueous dispersion that can provide a coating with excellent film-formation properties, clear-coat transparency, adhesion and weather resistance, as well as high gloss and excellent mechanical characteristics, a water-based paint containing this dispersion and a coated material.



[0008]

The inventors of the present invention arrived at the present invention upon discovering that the aforementioned objectives can be reached by means of an aqueous dispersion that is compatible at a molecular level, produced by the seed polymerization of determinate amounts of acrylate alkyl ester and/or methacrylate alkyl ester and ethylenic unsaturated monomer, and specifically, a monomer having cyclohexyl groups, in the presence of fluorine-containing polymer particles (referred to below as "seed particles"), and specifically, fluorine-containing polymer particles which have a specific composition containing 70-95% (mol%, likewise below) of VdF and 5-30% of CTFE. In addition, the present invention was perfected on the basis of the discovery that there are extreme differences in adhesion improvement effects depending on whether cyclohexyl methacrylate and cyclohexyl vinyl ether are used, or whether the structurally similar n-hexyl methacrylate, isohexyl methacrylate, n-hexyl ether or isohexyl ether are used. Surprisingly, only monomers having cyclohexyl groups cause dramatic improvements in adhesion.

[0009]

Means to solve the problems

The present invention is a fluorine-containing polymer aqueous dispersion characterized by being produced by subjecting 20-100 parts by weight of a monomer mixture containing a acrylate ester with a C<sub>1-18</sub> alkyl group and/or a methacrylate alkyl ester

with a C<sub>1-18</sub> alkyl, and an ethylenic unsaturated monomer that can copolymerize with these esters, for emulsion polymerization in an aqueous medium in the presence of 100 parts by weight of fluorine-containing polymer particles, where the average particle diameter of the particles of polymers obtained by said emulsion polymerization is 0.05-3  $\mu$ m, and a monomer having cyclohexyl groups is contained in said ethylenic unsaturated monomer in the amount of 0.5-45 wt%, based on the weight standard of said monomer mixture.

[0010]

In addition, the present invention concerns a water-based paint that contains the aforementioned fluorine-containing polymer aqueous dispersion.

[0011]

In addition, the present invention concerns a painted material obtained by painting with the aforementioned aqueous paint.

[0012]

#### Function and application examples

Examples of the fluorine-containing polymer that is used as seed particles in the present invention include chlorotrifluoroethylene (CTFE), tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinylidene fluoride, trifluoroethylene

(TrFE), vinyl fluoride (VF) and other simple monomers or copolymers, or copolymers of these monomers with other ethylenic unsaturated monomers that are copolymerizable therewith, such as cyclohexyl vinyl ether (CHVE), ethyl vinyl ether (EVE) and other vinyl ether monomers. Of these substances, CTFE/vinyl ether copolymers and VdF copolymers are preferably used from the standpoint of compatibility with the acrylic resin. In addition, among these copolymers, VdF copolymers are preferred, and in such a case, a copolymer is optimal that contains 70-95% VdF and 5-30% CTFE, with 75-90% VdF and 10-25% CTFE being preferred, and 75-85% VdF and 15-25% CTFE being particularly desirable.

[0013]

When VdF is present at 70 mol% or greater, the compatibility of the seed particles with the monomer mixture composed of acrylate alkyl ester and/or methacrylate alkyl ester and ethylenic unsaturated monomer is improved, the transparency of the film formed by drying the emulsion (referred to below as "cast film") and the mechanical characteristics are excellent, and excellent characteristics are obtained due to the so-called compatibility. In addition, if the amount of CTFE is less than 5 mol%, there are cases in which the solubility of the seed particles in the monomer mixture composed of acrylate alkyl ester and/or methacrylate alkyl ester and ethylenic unsaturated monomer decrease, cases in which swelling of the seed particles with the monomer mixture during seed polymerization do not occur very quickly, cases in which the transparency of the cast film obtained from the emulsion decrease transparency, and cases in

CTFE/VdF  
are preferred  
as seed latex

VdF > 70%  
CTFE > 5%  
for good  
compatibility  
with  
acrylic mono-  
mer mixture

which the gloss and adhesive properties are not readily manifested during the production of a coating from the paint.

[0014]

The content of ethylenic unsaturated monomer that is copolymerizable with the aforementioned monomer such as VdF or CTFE is 0-30%, with 10-25% being preferred and 10-20% being more desirable.

TFE  
0-20%  
more desirable.

[0015]

When the seed particles are composed of CTFE, VdF and TFE or VE, the solubility of the seed particles in the monomer improve, and during seed polymerization, swelling of the seed particles with the monomer rapidly occurs. In addition, the cast films formed from the resulting emulsion have improved transparency, and good gloss is obtained during preparation of a coating from the paint.

[0016]

In addition, when the seed particles are composed of CTFE, VdF and HFP or TrFE, the seed particles readily dissolve in the monomer, and the solubility of the HFP, TrFE and acrylic and/or methacrylic copolymer improve. Moreover, the cast film obtained from the resulting emulsion has improved transparency, and a coating with high gloss is obtained.

[0017]

The average particle diameter of the fluorine-containing polymer in the present invention is closely related to the average particle diameter of the fluorine-containing polymer obtained after seed polymerization. In order that the average particle diameter of the fluorine-containing polymer after seed polymerization is 0.05-3  $\mu\text{m}$ , with 0.05-0.5  $\mu\text{m}$  being preferred, and 0.1-0.2  $\mu\text{m}$  being more desirable, the average particle diameter should be 0.05-2.8  $\mu\text{m}$ , with 0.05-0.48  $\mu\text{m}$  being preferred, and 0.09-0.18  $\mu\text{m}$  being more desirable.

particle  
size distribution  
recommended

[0018]

The fluorine-containing polymer that is used for the seed particles is obtained by a common emulsion polymerization method, as was stated above.

[0019]

For example, the substance can be prepared by the emulsion polymerization of a monomer mixture containing fluoro-olefin in the presence of a fluorine-based reactive emulsifier having hydrophilic moieties in the amount of 0.01-1.0%, and in the presence of a fluorine-based emulsifier in the amount of 0.1-1.0%.

[0020]

In addition, the substance can also be prepared by the emulsion polymerization of a monomer mixture containing fluoro-olefin, in the presence of 1.0 wt% or less of a fluorine surfactant with respect to the amount of water, with 0.5 wt% or less being preferred, and 0.2 wt% or less being particularly desirable (with the lower limit generally being 0.01 wt%), and 0.001-0.1 wt% of a nonionic fluorine-based surfactant with respect to the amount of water, with 0.01-0.05 wt% being preferred.

[0021]

The aqueous dispersion that is obtained by these methods can contain seed particles with an average particle diameter of 0.2  $\mu\text{m}$  or less at a high concentration of 30-50 wt% while remaining stable.

[0022]

Examples of the aforementioned fluorine-based reactive emulsifiers having hydrophilic moieties include substances having structures expressed by  $\text{CF}_2=\text{CF}-(\text{CF}_2\text{CFX})_n\text{Y}$  (in the formula, X denotes F or  $\text{CF}_3$ , Y denotes  $\text{SO}_3\text{M}$  or  $\text{COOM}$  (where M denotes a hydrogen atom, amine, ammonium or alkali metal atom) and n denotes a positive integer),  $\text{CF}_2=\text{CF}-\text{O}(\text{CFX})_n\text{Y}$  (in the formula, X, Y and n are the same as above),  $\text{CH}_2=\text{CF}-\text{CF}_2-\text{O}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n-\text{CF}(\text{CF}_3)\text{Y}$  (in the formula, Y and n are the same as above) and  $\text{CF}_2=\text{CF}-\text{CF}_2-\text{O}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n-\text{CF}(\text{CF}_3)\text{Y}$  (in the formula, Y and n are

the same as above). It is preferable for  $n$  to be in the range of 0-3 from the standpoint of solubility in water and surface activity.

[0023]

More specifically, substances can be used where  $n$  is 0-2 in the structure  $\text{CH}_2=\text{CF}-\text{CF}_2-\text{O}((\text{CF}_3)\text{CFCF}_2\text{O})_n-(\text{CF}_3)\text{CFCOOH}$ .

[0024]

The polymerization temperature is 20-120°C, with 30-70°C being preferred. If the polymerization temperature is lower than 20°C, the stability of the resulting latex decreases, whereas if the polymerization temperature is higher than 120°C, there is a tendency towards a decrease in the rate of polymerization due to chain transfer. Although polymerization depends on the type of polymers, ordinarily, the reaction is carried out for 5-100 h while heating under a pressure of 1.0-50 kgf/cm<sup>2</sup> (gage pressure).

[0025]

The aforementioned fluorine-based emulsifier that is used in the emulsion polymerization of the seed particles can be used alone or as a mixture of numerous types of surface-active compounds containing fluorine atoms within the structure. Examples include acids expressed by  $\text{X}(\text{CF}_2)_n\text{COOH}$  (where  $n$  denotes a positive integer of 6-20 and  $\text{X}$  denotes F or H), and alkali metal salts, ammonium salts, amine salts and quaternary ammonium salts thereof or acids expressed by  $\text{Y}(\text{CH}_2\text{CF}_2)_m\text{COOH}$  (where  $m$

denotes a positive integer of 6-13 and Y denotes F or Cl), and alkali metal salts, ammonium salts, amine salts of quaternary ammonium salts thereof. More specifically, ammonium salts of perfluorooctanoic acid and ammonium salts of perfluorononanoic acid can be used. In addition, common fluorine-based surfactants can also be used.

[0026]

In emulsion polymerization that is carried out in order to produce seed particles, small amounts of nonionic fluorine-based surfactant can be used in the presence of the fluorine-based surfactant, and specific examples include polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene alkyl esters, sorbitan alkyl esters, polyoxyethylene sorbitan alkyl esters, glycerin esters and derivatives thereof. More specific examples include, with regard to polyoxyethylene alkyl ethers, polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether and polyoxyethylene behenyl ether; with regard to polyoxyethylene alkyl phenyl ethers, polyoxyethylene nonylphenyl ether and polyoxyethylene octylphenyl ether; with regard to polyoxyethylene alkyl esters, polyethylene glycol monolaurate, polyethylene glycol monooleate, and polyethylene glycol monostearate; with regard to sorbitan alkyl esters, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate and polyoxyethylene sorbitan monooleate; with regard to polyoxyethylene sorbitan alkyl esters, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, and polyoxyethylene



sorbitan monostearate; and with regard to glycerin esters, glyceryl monomyristate, glycerin monostearate and glycerin monooleate. In addition, examples of derivatives thereof include polyoxyethylene alkyl amines, polyoxyethylene alkylphenyl formamide condensation products and polyoxyethylene alkyl ether phosphates. Particularly desirable examples are polyoxyethylene alkyl ethers and polyoxyethylene alkyl esters with HLB values of 10-18. Specific examples are polyoxyethylene lauryl ether (EO: 5-20, where EO denotes the number of ethylene oxide units), polyethylene glycol monostearate (EO: 10-55) and polyethylene glycol monooleate (EO:6-10).

[0027]

In the present invention, the monomer mixture containing the acrylate alkyl ester and/or methacrylate alkyl ester and ethylenic unsaturated monomer is subjected to seed polymerization in the presence of seed particles.

[0028]

Examples of acrylate alkyl esters with  $C_{1-18}$  alkyl groups having in the present invention include methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-amyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate and lauryl acrylate. Of these substances, acrylate alkyl esters having  $C_{1-13}$  alkyl groups are preferred, and acrylate alkyl esters having  $C_{1-2}$  alkyl groups are particularly desirable. These monomers can be used individually or in mixtures of two or more types.

[0029]

In addition, examples of the aforementioned methacrylate alkyl esters having C<sub>1-18</sub> alkyl groups include methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-amyl methacrylate, isoamyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate and lauryl methacrylate. Of these substances, acrylate alkyl esters having C<sub>1-3</sub> alkyl groups are preferred, and acrylate alkyl esters having C<sub>1-2</sub> alkyl groups are particularly desirable. These monomers can be used individually or in mixtures of two or more types.

[0030]

In the present invention, when the aforementioned alkyl acrylate and the aforementioned alkyl ester methacrylate are used in conjunction, there are no restrictions on the ratio of the two substances, and appropriate selections can be made in accordance with the desired characteristics of the aqueous dispersion of the polymer particles.

[0031]

Examples of ethylenic unsaturated monomers that can be copolymerized with acrylate alkyl esters and/or methacrylate alkyl esters include vinyl compounds, and specifically, monomers having cyclohexyl groups.

[0032]

Examples of vinyl compounds in the present invention include acrylamide, methacrylamide, N-methylacrylamide, N-methylmethacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N-alkylacrylamide, N-alkylmethacrylamide, N,N-dialkylacrylamide, N,N-dialkylmethacrylamide and other amide compounds, 2-hydroxyethyl acrylate, N,N-dialkylaminoethyl acrylate, glycidyl acrylate, fluoroalkyl acrylate and other acrylate esters, 2-hydroxyethyl methacrylate, N,N-dialkylaminoethyl methacrylate, glycidyl methacrylate (GMA), fluoroalkyl methacrylate, ethylene glycol dimethacrylate and other methacrylate esters, allylglycidyl ether and other vinyl ether compounds, 1,3-butadiene, isoprene, chloroprene and other conjugated dienes, styrene,  $\alpha$ -methylstyrene, halogenated styrene, divinylbenzene and other aromatic vinyl compounds, and acrylonitrile, methacrylonitrile and other vinyl cyanide compounds. These monomers can be used individually or in mixtures of two or more types.

[0033]

In addition, examples also include vinyl ester compounds such as Veova 9 and Veova 10 (Shell Chemical), which are vinyl ester mixtures having branched alkyl groups.

[0034]

Examples of monomers having cyclohexyl groups include cyclohexyl acrylate (CHA), cyclohexyl methacrylate (CHMA) and

cyclohexyl vinyl ether (CHVE), but CHMA and CHVE are preferred from the standpoint of weather resistance.

[0035]

The amount used of the aforementioned monomer having cyclohexyl groups is 0.5-45 wt% with respect to the total of the monomer mixture of acrylic acid alkyl ester and/or methacrylate alkyl ester and the ethylenic unsaturated monomer, with 1-20 wt% being preferred. If this amount is less than 0.5 wt%, good paint composition adhesion to base materials, which is one of the objectives of the present invention, is not adequate. If this amount exceeds 45 wt%, the compatibility with seed particles is poor, the transparency of the dried film formed from the aqueous dispersion decreases, and the elongation and elasticity and other dynamic characteristics of the film decrease. In addition, the gloss of the coating decreases, and the weather resistance of the film tends to decrease.

CHMA  
and  
CHVE  
being  
preferred.  
0.5-45wt%  
with  
1-20wt%  
preferred.

[0036]

The total of the amounts used of the aforementioned ethylenic unsaturated monomer and the acrylate alkyl ester and/or methacrylate alkyl ester is 20-100 parts (parts by weight, likewise below) with respect to 100 parts of the seed particles, with 30-100 parts being preferred, and 40-100 parts being more desirable. If this amount is less than 20 parts, there is a tendency towards decreases in transparency, gloss and adhesion during film formation. If this amount exceeds 100 parts, there is a tendency towards decreased weather resistance.

Acrylic/Vinyl  
20-100 parts.  
Thioest  
100 parts  
soft  
20-50%  
acrylic  
<20%  
>50% loss in weather resistance.

[0037]

Seed polymerization of the acrylate alkyl ester and/or methacrylate alkyl ester with the ethylenic unsaturated monomer can be carried out under the same conditions that are used for common emulsion polymerization. For example, the reaction can be carried out for 0.5-6 h at a temperature of 20-90°C, with 20-80°C being preferred and 30-70°C being more desirable in an aqueous medium containing the seed particles, after adding surfactant, polymerization initiator, chain transfer agent, and as necessary, chelation agents, pH adjusters and solvents.

*Temperature  
higher Polymer  
- just -*

[0038]

In terms of seed polymerization, a method can be used wherein all of the monomer of the reaction system is added to the seed particles at the same time, or a method can be used wherein some of the monomer is added and allowed to react, whereupon the remainder of the monomer is added continuously or in divided amounts. A method can also be used wherein all of the monomer is added continuously.

*monomer  
added  
strategy*

[0039]

When seed polymerization of the acrylate alkyl ester and/or methacrylate alkyl ester and the ethylenic unsaturated monomer is carried out by means of emulsion polymerization in the presence of seed particles, first, swelling of the seed particles with the monomers is carried out, and at this point, the seed particles are uniformly dissolved in the monomers in the form of an aqueous

*seed  
time*

dispersion. By then adding a polymerization initiator, the monomers are polymerized, and compatible particles are formed wherein the molecular chains are crosslinked. In addition, by the copolymerization of a polyfunctional monomer, an interpenetrating network structure (IPN) can be formed. Examples of polyfunctional monomers include monoglycol dimethacrylate or diglycol dimethacrylate.

[0040]

Examples of surfactants that are used in seed polymerization include anionic surfactants and nonionic surfactants, or combinations thereof, as well as amphoteric surfactants. Examples of anionic surfactants include higher alcohol sulfate esters, such as sodium alkyl sulfonate, sodium alkylbenzenesulfonate, succinic acid dialkyl ester sodium sulfonate and alkyldiphenyl ether sodium disulfonate. Examples of nonionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene alkyl esters, polyoxyethylene alkylphenyl esters, sorbitan alkyl esters, glycerin esters and derivatives thereof. An example of an amphoteric surfactant is lauryl betaine. In addition, so-called reactive emulsifiers that can copolymerize with acrylate esters, methacrylate esters or ethylenic unsaturated monomers such as stainless [sic] sodium sulfonate and sodium alkylsulfosuccinate can also be used. The amount used of surfactant is ordinarily about 0.05-5.0 parts with respect to a total of 100 parts of the acrylate alkyl ester and/or methacrylate alkyl ester and the ethylenic unsaturated monomer.

reg. linking  
of the core  
after soak time  
→ IPN

[0041]

There are no particular restrictions on the polymerization initiator, provided that it generates radicals that can undergo free radical reactions in aqueous solvents between 20 and 90°C. In some cases, the substance can be used in combination with reducing agents. Examples of aqueous polymerization initiators that are commonly used include persulfates and hydrogen peroxide, and examples of reducing agents include sodium pyrobisulfite, sodium bisulfite, and sodium L-ascorbate. Examples of oil-soluble polymerization initiators include diisopropyl peroxydicarbonate (IPP), benzoyl peroxide, dibutyl peroxide and azobisisobutyronitrile (AIBN). The amount of polymerization initiator used is generally about 0.05-2.0 parts with respect to a total of 100 parts of the acrylate alkyl ester and/or methacrylate alkyl ester and the ethylenic unsaturated monomer.

[0042]

The polymerization temperature should be in the range of 20-90°C, with 30-70°C being preferred.

[0043]

Examples of chain transfer agents include halogenated hydrocarbons (such as chloroform or carbon tetrachloride) and mercaptans (such as n-dodecyl mercaptan, t-dodecyl mercaptan, n-octylmercaptan and thioglycolate isooctyl ester). Of these substances, it is preferable to use thioglycolate isooctyl ester and n-dodecyl mercaptan from the standpoint of chain transfer

effects and odor. The amount of chain transfer agent used is normally about 0-5.0 parts per total of 100 parts of the acrylate alkyl ester and/or methacrylate alkyl ester and the ethylenic unsaturated monomer.

[0044]

Examples of solvents that can be used include small amounts of methyl ethyl ketone, acetone, trichlorotrifluoroethane, methyl isobutyl ketone and ethyl acetate in ranges in which the workability, fire safety, environmental safety and structural stability are not adversely affected. There are cases where the swelling properties of the monomer with respect to the seed particles are improved by the addition of solvent.

[0045]

The fluorine-containing polymer aqueous dispersion of the present invention is obtained in the manner described above, but from the standpoint of improving the film-formation properties and adhesion properties, which is an objective of the present invention, it is desirable to subject the methacrylate alkyl ester and monomer copolymerizable therewith for seed polymerization in the presence of an aqueous dispersion containing fluorine-containing polymer particles having a Tg of anywhere from -35°C to 25°C. By this means, the minimum film-formation temperature of the fluorine-containing copolymer aqueous dispersion can be freely set in the range of 0-70°C by selecting the Tg of the aforementioned seed particles.

improved  
swelling  
by adding  
solvent.



[0046]

Methacrylate alkyl esters with a C<sub>1-6</sub> side chain are preferred because they have little effect in terms of decreasing weather resistance, but as the carbon number of the side chain decreases, the compatibility with VdF copolymer resins increases. It is thus more preferable to use methacrylate alkyl esters with a C<sub>1-3</sub> side chain, with methyl methacrylate having a C<sub>1</sub> side chain being more desirable.

better  
for compatib.  
with  
VdF copolymer

[0047]

In addition, a polyfunctional monomer such as ethylene glycol dimethacrylate or propylene glycol dimethacrylate can be copolymerized in order to improve the solvent resistance and water resistance of the material.

[0048]

During emulsion polymerization carried out in the presence of aqueous dispersed particles, a compound wherein hydrophilic moieties are contained in the molecules of a low molecular weight polymer or oligomer can be used as the monomer that has ethylenic unsaturated bonds that can be copolymerized. The aforementioned hydrophilic moieties denote hydrophilic bonds or moieties having hydrophilic groups. Examples of hydrophilic groups include anionic, nonionic or amphoteric groups, or any combination thereof, but nonionic and anionic hydrophilic groups are preferred. Moreover, known reaction emulsifiers can also be present.

[0049]

Examples of the aforementioned monomers and reactive emulsifiers include commercially available substances such as Burenma [transliteration] PE-350, Burenma PME-400, Burenma 70PEP350B, Uniox PKA5002, Uniox PKA5003, Uniox PKA5004 (Nippon Yushi), NK ester M-40G, NK ester M-90G, NK ester M-230G, NK ester AMP-60G, NK ester CB-1, NK ester SA, NK ester A-SA (Shin-Nakamura Kagaku), and Ereminoru [transliteration] JS2 and Ereminoru RS30 (Sanyo Kasei Kogyo).

[0050]

Of the aforementioned monomers, allyl ether derivatives that do not have detrimental influences such as decreasing weather resistance are preferred.

[0051]

The average particle diameter of fluorine-containing polymer particles in the aqueous dispersion obtained by seed polymerization in the present invention should be 0.05-3  $\mu\text{m}$ , with 0.05-0.5  $\mu\text{m}$  being preferred and 0.1-0.2  $\mu\text{m}$  being particularly desirable. If the average particle diameter is less than 0.05  $\mu\text{m}$ , the viscosity of the aqueous dispersion increases, and a high-temperature aqueous dispersion is not obtained. If the average particle diameter of the fluorine-containing polymer particles is greater than 3  $\mu\text{m}$ , sedimentation of the particles occurs during storage of the aqueous dispersion and aggregation also occurs.

Moreover, there is the problem of a lack of gloss during coating preparation.

[0052]

The fluorine-containing polymer aqueous dispersion composition of the present invention can be used as a water-based paint, or as a coating material for coated paper or as a protective coating for surfaces such as concrete by blending additives commonly used in aqueous emulsion paints such as pigments, thickeners, dispersing agents, anti-foaming agents, freeze prevention agents and film-formation aids.

[0053]

In addition, the fluorine-containing polymer aqueous dispersion composition of the present invention can also be used as an interior and/or exterior water-based paint for buildings and structures.

[0054]

Conventional known coating methods can be used as the method for coating the water-based paint of the present invention. Conventional known coating devices such as brushes, rollers, roller coaters, air sprayers, airless sprayers, electrostatic coaters, immersion coaters and electrophoretic coaters can be used for coating.

[0055]

The water-based paint of the present invention is appropriate for use with various types of base materials such as iron, aluminum, copper or alloys thereof and other metals, as well as glass, cement, concrete and other inorganic materials, FRP, acrylic resin vinyl chloride resin, polycarbonate resin, polyurethane resin and other resins, wood and fiber. In addition, a preparative treatment or surface treatment can be carried out on the base material as necessary, and the paint composition of the present invention can be applied after an appropriate undercoat or precoat. The coating is hardened by drying for 30 sec to 1 week at 5-300°C, depending on the type of hardener. There are no particular restrictions on the coating film thickness, but ordinarily, the thickness is 1-200  $\mu\text{m}$ , with 5-100  $\mu\text{m}$  being preferred and 10-50  $\mu\text{m}$  being more desirable.

[0056]

The coating obtained in this manner has excellent adhesive properties, weather resistance and chemical resistance, and the coated surface can be used in a wide range of applications due to its smoothness. Specifically, the material can be used in a wide range of applications including the interior or exterior decoration of electric products (electronic ranges, toasters, refrigerators, washing machines, hair dryers, televisions, video recorders, amplifiers, radios, electric pots, thermoses, radio cassette players, cassette decks, compact disc players and video cameras), the interior or exterior decoration of indoor air conditioners, outdoor air conditioners, air vents and ducts, air

filters and other air conditioning devices, the interior or exterior decoration of fluorescent lamps, chandeliers, reflective plates and other illumination devices, household tools, mechanical parts, decorations, combs, glasses frames, natural fibers, synthetic fibers (yarn materials and knits formed from these materials) and office equipment (telephones, facsimile machines, copiers (including rollers), photographic equipment, overhead projectors, objective cameras, watches, slide projectors, desks, bookshelves, lockers, document shelves, chairs, bookends, electronic chalkboards), as coatings for automobiles (wheels, door mirrors, chenille, door knobs, license plates, handles, and instrument panels), or kitchen equipment (range hoods, sink racks, kitchen tables, kitchen knives, cutting boards, water faucets, gas ranges and fan blades), for the interior decorative painting of partitions, bath units, shutters, blinds, curtain rods, accordion curtains, walls, ceilings and floors, and the outdoor decoration of outer walls, railings, entranceways, shutters and other common external fixtures for houses and buildings, as well as for exterior construction materials such as fired siding materials, foam concrete panels, concrete panels, curtain walls, vinyl chloride, steel plates and sheets, as well as window glass.

[0057]

The present invention is described below using application examples, but the present invention is not restricted to these application examples.

[0058]

Synthesis Example 1

500 mL of deionized water, 0.5 g of ammonium perfluorooctanoic acid and 0.5 g of reactive emulsifier having a structure expressed by  $\text{CH}_2=\text{CF}-\text{CF}_2-\text{OCF}(\text{CF}_3)\text{CF}_2\text{O}-\text{CF}(\text{CF}_3)\text{COOH}$  were introduced into a pressure-tight reaction vessel with an inner volume of 1 L, and after introducing nitrogen under pressure and removing the residual air by repeating degassing, the vessel was pressurized to 8 kgf/cm<sup>2</sup> at 60°C with a monomer mixture having a VdF/TFE/CTFE mole ratio of 74/14/12 mol%. Next, 1.5 g of ethyl acetate was introduced under pressure, and 0.2 g of ammonium persulfate was added. Said monomer mixture was continuously supplied so that the pressure on the interior of the vessel was 8 kgf/cm<sup>2</sup>, and a reaction was allowed to occur for 45 h. The interior of the vessel was then returned to ambient pressure and temperature in order to complete the reaction.

[0059]

The aqueous dispersions were subjected to the measurements described below.

[0060]

Solid concentration: The substance was dried at 150°C in a vacuum dryer, and the weight after drying was expressed as a percentage of the weight of the aqueous dispersion before drying.

[0061]

Average particle diameter: Measured using a laser light scattering particle diameter measurement device (ELS-3000, manufactured by Otsuka Denshi).

[0062]

The results are shown in Table I.

[0063]

#### Synthesis Examples 2-5

With the exception that the composition of the monomer mixture in Synthesis Example 1 was changed as indicated in Table I, synthesis was carried out by the same method as in Synthesis Example 1 to obtain the aqueous dispersions of Synthesis Examples 2-5. The same measurements as in Synthesis Example 1 were carried out and the results are shown in Table I.

[0064]

#### Synthesis Example 6

20.0 g of cyclohexyl vinyl ether (CHVE) having the composition shown in Table I, 11.4 g of ethyl vinyl ether (EVE), 4.5 g of macromonomer having hydrophilic moieties (PKA5003, Nippon Yushi-type), 66.1 g of deionized water, 0.35 g of ammonium perfluorooctanoate (emulsifier), 0.35 g of potassium carbonate

( $K_2CO_3$ ), 0.02 g of sodium bisulfite ( $NaHSO_3$ ) and 0.08 g of ammonium persulfate (initiator) were introduced into a 200-mL autoclave equipped with a stainless steel stirrer, and after chilling with ice, nitrogen gas was introduced to a pressure of  $3.5 \text{ kg/cm}^2$ , whereupon the gas was removed. This pressurization and degassing process was repeated twice, whereupon the vessel was evacuated to 10 mm Hg in order to remove the residual oxygen. 38.0 g of chlorotrifluoroethylene (CTFE) was then introduced, and a reaction was allowed to occur for 12 h at  $30^\circ\text{C}$  to obtain the aqueous dispersion of Synthesis Example 6. The same measurements as in Synthesis Example 1 were carried out, and the results are shown in Table I.

[0065]

Table I

		① 合成例					
		1	2	3	4	5	6
② 単量体 仕込量 (モル%)	VdF	74	78	55	68	97	
	TFE	14	16		20		
	CTFE	12			12	3	50
	HFP		6	45			
	CHVE						25
	EVE						25
③ 水性分散液	④ 固形分濃度 (%)	40	40	35	35	30	50
	⑤ 平均粒子径 ( $\mu\text{m}$ )	0.12	0.13	0.10	0.13	0.14	0.18
	⑥ 反応時間 (hr)	45	43	36	30	48	12

VdF/TFE/CTFE

VdF/TFE/HFP

③ VdF/HFP (55/45)  $\rightarrow$  35%

VdF/CTFE (

⑥ CTFE/CHVE/EVE  $\rightarrow$  total 50%

50

50%



Key	1	Synthesis example
	2	Introduced amount of monomer (mol%)
	3	Aqueous dispersion
	4	Solids content (wt%)
	5	Average particle diameter ( $\mu\text{m}$ )
	6	Reaction time (h)

[0066]

#### Application Example 1

70 g of the aqueous dispersion obtained in Synthesis Example 1 are introduced into a four-necked flask with an inner volume of 200 mL equipped with a stirrer, cooling jacket and temperature gage. 0.5 wt% of JS2 (manufactured by Sanyo Kasei Kogyo) was then added with respect to the solid content in said aqueous dispersion, and the reaction was heated on a water bath while stirring. At the point when the vessel temperature reached 80°C, an emulsion produced by emulsifying 10 g of methyl methacrylate (referred to below as "MMA"), 1.2 g of cyclohexyl methacrylate (referred to below as "CHMA"), 1.5 g of PKA5003 (Nippon Yushi) and 0.3 g of isooctyl thioglycolate ester in a 0.5 wt% aqueous solution of JS2 (manufactured by Sanyo Kasei Kogyo) was added dropwise over 1 h. Immediately afterwards, 1 mL of a 2 wt% aqueous solution of ammonium persulfate was added and the reaction was initiated. 3 h after initiation of the reaction, the temperature in the vessel was increased to 85°C and was maintained for 1 h before being cooled. The pH was then adjusted to 7 with aqueous ammonia, and the material was then filtered with a 300-mesh metal screen to obtain a bluish-white aqueous dispersion composition of a fluorine-containing polymer.

[0067]

The following tests were carried out on the aqueous dispersion.

[0068]

(1) Evaluation of aqueous dispersion characteristics  
Solids concentration and average particle diameter: Same as above.

Minimum film-formation temperature (MFT): A thermogradient tester manufactured by Rikagaku Kogyo) was used, and the minimum temperature at which a continuous film formed was measured.

[0069]

(2) Evaluation of dried film formed from the aqueous dispersion

The aqueous dispersion was poured into a petri dish with a diameter of 10 cm to produce a dry film thickness of 200  $\mu\text{m}$ , and drying was carried out for 24 h at 80°C. The light transmissivity of the film was then measured at a wavelength of 800 nm, and the materials were evaluated as indicated below:

[0070]

- A: Transmissivity of 90% or greater
- B: Transmissivity of 80-90%
- C: Transmissivity of 60-80%
- D: Transmissivity of less than 60%

Dynamic characteristics of the dry film formed from the aqueous dispersion

The aforementioned dried film was cut into #2 dumbbells according to JIS K6301, and the elongation and elastic modulus were measured.

[0071]

### (3) Evaluation of coating characteristics

50 parts of titanium oxide filler (product name CR90 (manufactured by Sekigen Sangyo)), 2 parts of Nobukosubasu [transliteration] SN5027 dispersing agent (manufactured by Sannobuko), 1 part of ethylene glycol antifreeze agent, 0.5 part of FS antifoam 013B antifoaming agent (manufactured by Nippon Nyukazai), 0.5 part of UH420 thickener (manufactured by Asahi Denka Kogyo) and 15 parts of Texanol CS12 film-formation aid (manufactured by Chisso) were added with respect to 100 parts of the solids content of the aqueous dispersion obtained in Application Example 1. The substances were mixed well using a dispersing stirrer to prepare a paint.

Texanol  
15%

[0072]

#### Initiation

Gloss: The paint was spread on an aluminum plate using an applicator to produce a film thickness of 20  $\mu\text{m}$ , and after drying for 1 week at room temperature, the gloss was measured at a reflection angle of 60° using a gloss meter (Suga Shikenki).

[0073]

Pencil hardness: The film hardness of the film obtained on the aforementioned aluminum plate was measured according to the JISK5400 pencil hardness test.

[0074]

#### Adhesive properties

The aqueous dispersion of Application Example 1 was used, and the paint prepared as described above was applied (1) using an applicator onto a slate board coated with Mobiniru [transliteration] 940 aqueous acrylic sealer (manufactured by Hekisuto Gosei) so that the thickness of the coating was 40  $\mu\text{m}$ , before being dried for one week at room temperature, and (2) using an air spray gun onto a slate board coated with elastic acrylic sealer Haipurufu [transliteration] medium coat (manufactured by Nippon Tokushu Toryo) so that the thickness of the coating was 40  $\mu\text{m}$ , before being dried for 1 week at room temperature. Following the method of JIS K 5400, squares consisting of 25 frames at a spacing of 2 mm were produced on each of the materials, and a tape peeling test was carried out. The number of remaining squares was determined for each sealer, and the results are shown in Table II.

[0075]

#### Water immersion test

The aforementioned various sealers were applied and the resulting coated boards were immersed in deionized water for 10 days at room temperature. The boards were removed and were dried for 1 day, before being measured in terms of gloss and adhesion by means of the same methods as described above.

[0076]

#### Accelerated weather resistance test

The test boards used in the aforementioned gloss measurements produced by coating 20- $\mu$ m films on aluminum plates with an applicator were exposed for 1000 h with an Aisupa [transliteration] UV tester (SUV) (manufactured by Iwazaki Denki). The gloss was then measured and the percentage of the initial gloss was expressed as the gloss retention ratio (%). In addition, coated plates formed by applying (1) the acrylic sealer and (2) the elastic sealer produced in the adhesion test were exposed for 1000 h with an SUV, and the adhesion was measured in the same manner as described above.

[0077]

The results are shown in Table II.

[0078]

## Application Examples 2-14

The aqueous dispersions of the synthesis examples and the monomer mixtures shown in Table II were used, and seed polymerization was carried out by the same methods as in Application Example 1 to produce the aqueous dispersions of Application Examples 2-14. Testing was carried out in the same manner as in Application Example 1. The results are shown in

[0079]

Table II

		① 比較例										
② 合成例番号		1	2	3	4	5	6	7	8	9	10	11
③ 単量体 (重量部)		43	100	17	110	0	43	43	43	43	43	43
④ 単量体混合割合 (wt %)	MMA	100	48	90	90		90	90	90	90	90	90
	EA											
	CHMA		52	10	10							
	CHA											
	CHVE											
	nHMA						10					
	nHVE							10				
	HEMA								10			
	GMA									10		
	MSiMA										10	
⑤ 水性分散液	固形分濃度 (%)	46	46	41	49	50	46	46	46	46	46	46
	平均粒子径 (μm)	0.15	0.15	0.13	0.17	0.18	0.15	0.15	0.15	0.15	0.15	0.15
	最低成膜温度 (°C)	36	52	34	54	35	35	34	38	37	42	44
⑥ 水性分散液乾燥膜	透明性 (10)	A	D	A	A	A	A	A	A	A	A	A
	伸び (×102%) (11)	3.2	2.5	2.3	1.9	2.0	3.2	3.0	2.5	2.7	2.3	1.9
	弾性率 (12)	1.3	3.1	1.5	3.2	0.3	1.2	1.2	2.3	1.3	1.5	2.6
⑦ 塗膜特性	⑧ 初期光沢 (5)	74	48	36	78	74	72	73	68	70	67	61
	⑨ 耐擦度 (16) (18)	HB	H	F	H	B	F	F	HB	F	H	H
	⑩ 密着性 (17) アクリルシーラー (19)	18	23	15	25	20	17	12	25	23	15	25
	⑪ 密着性 (17) 弾性シーラー (19)	6	21	10	25	12	11	8	24	21	10	25
	⑫ 水浸漬試験後光沢 (5) (18)	73	52	35	70	70	70	72	68	69	65	69
	⑬ 密着性 (17) アクリルシーラー (19)	5	20	10	25	5	0	0	0	12	0	10
	⑭ 密着性 (17) 弾性シーラー (19)	0	19	0	25	2	0	0	0	3	0	4
	⑮ 耐熱性試験後光沢保持率 (5) (18)	90	69	81	47	87	83	83	76	71	67	62
	⑯ 密着性 (17) アクリルシーラー (19)	0	20	10	25	0	0	0	0	10	0	6
	⑰ 密着性 (17) 弾性シーラー (19)	0	19	0	25	0	0	0	0	5	0	12

②③④ MMA/CHMA

⑥ nHMA/MMA

Reactive monomers: HEMA/CHMA/MSiMA → Reproduction

Adhesive properties etc. seen after immersion in water for 10 days/RT

Key: 1	Application Examples
2	Synthesis example no.
3	Monomer (parts by weight)
4	Monomer mixture ratio (wt%)
5	Aqueous dispersion
6	Solid dispersion (%)
7	Average particle diameter ( $\mu\text{m}$ )
8	Minimum film-formation temperature ( $^{\circ}\text{C}$ )
9	Dried films formed from the aqueous dispersions
10	Transparency
11	Elongation ( $\times 10^2\%$ )
12	Elastic modulus
13	Coating characteristics
14	Initial
15	Gloss
$\propto$ 16	Pencil hardness
$\propto$ 17	Adhesive properties
18	Acrylic sealer
19	Elastic sealer
20	After water immersion test
21	After weather resistance test
22	Gloss retention
$\propto$ 22	Adhesive properties
22	Acrylic sealer

[0080]

The symbols in Table II denote the following monomers.

[0081]

- \*1) Methyl methacrylate
- \*2) Ethyl acrylate
- \*3) Cyclohexyl methacrylate
- \*4) Cyclohexyl acrylate

- \*5) Cyclohexyl vinyl ether
- \*6) Nonylhexyl methacrylate
- \*7) n-hexylvinyl ether
- \*8) Hydroxyethyl methacrylate
- \*9) Glycidyl methacrylate
- \*10)  $\gamma$ -trimethoxysilane methacrylate
- \*11) Methacrylic acid

As is clear from Table II, the adhesive properties with respect to base materials are superior for the paints obtained when seed polymerization was carried out using a monomer having cyclohexyl groups.

[0082]

#### Comparative Examples 1-11

Aqueous dispersions and monomers from the synthesis examples shown in Table III or mixtures thereof were used, and seed polymerization was carried out by the same method as in Application Example 1 to obtain the aqueous dispersions of Comparative Examples 1-11, which were then subjected to the same tests as in Application Example 1. However, only in Comparative Example 5 was seed polymerization not carried out. The results are shown in Table III. The symbols for the monomers were the same as in Table II.



[0083]

Table III

		① 実 施 例													
② 合成例番号		1	2	3	4	5	6	7	8	9	10	11	12	13	14
③ 単量体 (重量部)		43	43	43	43	20	43	43	43	100	43	43	43	43	43
④ 単量体 混合割合 (wt%)	MMA	90	90	90	80	99	96	70	55	95	90	90	90	90	90
	EA	10			10	1	5		45	5	10	10	10	10	10
④ 単量体 混合割合 (wt%)	CHMA		10												
	CHA			10				30							
④ 単量体 混合割合 (wt%)	CHVE														
	nHMA														
④ 単量体 混合割合 (wt%)	nHVE														
	HEMA														
④ 単量体 混合割合 (wt%)	GMA														
	MSiMA														
④ 単量体 混合割合 (wt%)	MA														
⑤ 水性 分散液	固形分濃度 (%)	48	48	45	46	42	48	48	45	48	45	40	41	35	52
	平均粒子径 (μm)	0.15	0.15	0.15	0.15	0.13	0.15	0.15	0.15	0.17	0.16	0.13	0.15	0.16	0.20
⑤ 水性 分散液	最低成膜温度 (°C)	36	32	33	29	28	36	33	45	62	40	45	38	34	58
④ 水性分散 液乾燥 フィルム	透明性 (15)	A	A	A	A	A	A	A	C	A	C	B	B	B	C
	伸び (×10 <sup>2</sup> %) (11)	3.0	3.3	2.8	3.6	2.5	3.1	2.1	1.8	2.0	2.2	2.5	2.0	2.3	1.4
④ 水性分散 液乾燥 フィルム	弾性率 (13)	1.2	1.0	1.1	1.0	1.2	1.3	1.5	1.8	3.1	0.8	1.2	1.2	0.8	0.6
⑬ 物理 特性	⑭ 初期 弾性率 (14)	73	73	74	74	62	75	70	57	76	58	58	56	55	50
	⑭ 初期 弾性率 (14)	HB	HB	HB	F	F	HB	H	H	H	F	F	F	F	F
⑬ 物理 特性	⑭ 初期 弾性率 (14)	25	25	25	25	20	25	25	25	25	25	25	25	25	25
	⑭ 初期 弾性率 (14)	25	25	25	25	20	25	25	25	25	25	25	25	25	21
⑬ 物理 特性	⑭ 初期 弾性率 (14)	72	73	74	73	60	75	70	60	72	58	58	58	58	52
	⑭ 初期 弾性率 (14)	25	25	25	25	20	25	25	25	25	25	25	25	25	19
⑬ 物理 特性	⑭ 初期 弾性率 (14)	25	25	25	25	19	25	25	25	25	25	25	25	25	13
	⑭ 初期 弾性率 (14)	88	81	90	76	87	90	82	71	67	69	62	72	73	53
⑬ 物理 特性	⑭ 初期 弾性率 (14)	25	25	25	25	20	25	25	25	25	25	25	25	25	21
	⑭ 初期 弾性率 (14)	25	25	25	25	20	25	25	25	25	25	25	25	25	14

- Key
- 1 Comparative Examples
  - 2 Synthesis Example No.
  - 3 Monomer (parts by weight)
  - 4 Monomer mixture ratio (wt%)
  - 5 Aqueous dispersion
  - 6 Solid dispersion (%)
  - 7 Average particle diameter (μm)
  - 8 Minimum film-formation temperature (°C)
  - 9 Dried films formed from the aqueous dispersions
  - 10 Transparency

- 11 Elongation ( $\times 10^2\%$ )
- 12 Elastic modulus
- 13 Coating characteristics
- 14 Initial
- 15 Gloss
- 16 Pencil hardness
- 17 Adhesive properties
- 18 Acrylic sealer
- 19 Elastic sealer
- 20 After water immersion test
- 21 After weather resistance test
- 22 Gloss retention

[0084]

As is clear from Table III, when a monomer having cyclohexyl groups is not used, the adhesive properties of the paint with respect to base materials is poor, and if the used amount of monomer having cyclohexyl groups exceeds 45%, the compatibility with the fluorine resin decreases, the transparency of the film formed by drying the aqueous dispersion is lost, and the gloss of the coating also decreases.

[0085]

In addition, it was found that if the amount of monomer mixture with respect to 100 parts by weight of fluorine-containing polymer particles exceeds 100 parts by weight, the gloss retention deteriorates, and the weather resistance is lost.

[0086]

Effect of the invention

The fluorine-containing polymer aqueous dispersion of the present invention can offer a coating that has superior film-formation properties, clear-coat transparency, adhesion and weather resistance, as well as high gloss and excellent mechanical characteristics.

[0087]

In addition, by using the aqueous paint of the present invention that contains the fluorine-containing polymer aqueous dispersion, a coating can be formed that has superior film-formation properties, adhesion, weather resistance and water resistance, as well as high gloss.

[0088]

In addition, the painted material obtained by painting the aforementioned aqueous paint of the present invention has a coating with superior adhesion, weather resistance, water resistance and gloss, and can be used in the numerous applications mentioned above.